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(54) WASHING AND CLEANSING COMPOSITIONS

- (71) We, **FARBWERKE HÖRCHST AKTIENGESELLSCHAFT**, vormals Meister Lucius & Brüning, a German Company of 6230 Frankfurt/Main 80, P.O. Box 800320, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to washing and cleansing compositions.

It has been proposed to increase the cleansing power of soaps and synthetic detergents in washing and cleansing compositions by the addition of certain substances called "builders". Washing and cleansing compositions that contain such builders have an increased cleansing power and are still cheaper than corresponding compositions without builders.

The mechanism and the different processes involved in the action of builders are not yet completely understood. There are several processes which play a role in the function of a builder, such as the stabilization of suspensions of pigmentary dirt, the emulsification of dirt particles, the influence on the surface-active and interfacial-active properties of aqueous surfactant solutions, the solubilization of water-insoluble components of the cleansing bath, the peptization of agglomerated dirt, the neutralization of acid substances and the inactivation of mineral substances in the washing bath.

In order to judge the quality and suitability of an individual substance as a builder, its behaviour and activity are tested in a washing or cleansing process. This ensures that all the factors which participate in the action of the builder will be taken into consideration both quantitatively and qualitatively.

Conventional builders are water-soluble in-

organic alkali metal salts, such as alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates. 45

In recent years, organic compounds having builder properties, such as water-soluble salts of monomeric compounds, for example amino-polycarboxylic acids and amino- and hydroxy-alkylidene-phosphonic acids, have been proposed but have not been used in practice. 50

U.S. Patent No. 3,308,067 describes water-soluble alkali metal, ammonium and substituted ammonium salts of homo- and copolymers of aliphatic polycarboxylic acids as builders for washing and cleansing compositions. As co-monomers, short-chain olefins and unsaturated carboxylic acids may be used. Of these polyelectrolyte builders, the sodium salt of polymaleic acid has been especially mentioned as having outstanding properties but these builders also have not found practical use. 55

Of the numerous products that have been proposed as builders, linear condensed phosphates or polyphosphates, especially pentasodium tri-phosphate and sodium tripolyphosphate are used almost exclusively in conventional washing and cleansing compositions, generally in quantities of up to about 50% by weight. Despite many advantages of the polyphosphates over other builders, some disadvantages have appeared during the long practical application of this type of builder. 65

The anhydride-like P—O—P bond in polyphosphates is relatively easily hydrolysed. Therefore especially in liquid detergents and cleansing agents, as well as in spray processes, decomposition products such as metaphosphates and ortho-phosphates are formed which have a very reduced activity. Undesired formation of turbidity or of precipitates may also occur in liquid compositions. 70

The polyphosphate content of washing and cleansing compositions has steadily increased in 75

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recent years and the domestic and industrial consumption of these compositions is also steadily increasing. Consequently the phosphate content in waste water is increasing and thus increases the risk of eutrophy, i.e. of over-fertilization. The growth of algae promoted thereby can become a risk for the other flora and fauna of lakes and rivers. It is, therefore, in general, desirable to lower the phosphate content of waste paper.

The present invention provides a washing or cleansing composition which comprises one or more anionic surfactants and/or one or more non-ionic surfactants and, as builder, one or more water-soluble neutral or acid salts of organic homo- or copolymers containing phosphonic acid groups and, advantageously, additionally containing carboxylic acid groups in the lateral chains. Water-soluble salts of polyvinylphosphonic acid or water-soluble salts of copolymers of vinylphosphonic acid with one or more other copolymerisable monomers, especially with acrylic acid, or mixtures of these salts are especially advantageous as builders for washing and cleansing compositions.

As water-soluble salts of the polymeric phosphonic acids, there may be used the alkali metal salts, the ammonium salts or substituted ammonium salts. As alkali metal salts, the sodium and potassium salts are advantageously used for economic reasons. The salts may be partially or fully neutralized.

As polymeric compounds to be used according to the present invention, those having a relative specific viscosity [RSV-value, measured in a 5% by weight solution of the free acid in a 10% aqueous sodium chloride solution of at least 0.020, preferably in the range of from 0.060 to 2.0] are advantageously used.

Homo- and copolymers of vinyl-phosphonic acid may be prepared according to known processes. Copolymers are prepared from at least 2% by weight, preferably from 5 to 60% by weight and especially from 30 to 55% by weight of vinyl-phosphonic acid or of a salt thereof. As copolymerizable compounds, there may be used, for example, acryl amide, crotonic acid and, especially, acrylic acid.

One process for the manufacture of the above homo- and copolymers is described, for example, in Belgian Patent No. 597,048. The homo- and copolymers may, however, especially advantageously be prepared by precipitative polymerization in solvents which dissolve the monomers but not the homo- and copolymers. Suitable solvents, are aliphatic carboxylic acids, preferably having from 1 to 6 carbon atoms, their anhydrides and their esters with alcohols having preferably up to 8 carbon atoms. Especially suitable solvents are, for example, formic acid, acetic acid, propionic acid, acetic anhydride and propionic anhydride, methyl, ethyl, propyl and butyl acetates and

methyl, ethyl, propyl and butyl butyrates. Mixtures of two or more solvents may also be used. Ethyl acetate is preferably used.

The quantitative proportion by weight of the solvent or solvent mixture to the mixture of monomers must be at least 2 : 1. In the case of a higher content of acrylic acid in the mixture of monomers it is suitable to use a higher proportion of from about 3 to 5 : 1. For carrying out the polymerization, the known initiators, for example azo compounds, peroxides, per-esters as well as redox systems may be used. Depending on the initiator system used, the polymerization temperature may be in the range of from room temperature to the boiling point of the solvent.

The following Examples illustrate a preferred method for preparing the copolymers. The parts and percentages are by weight.

(a) 70 parts of vinyl-phosphonic acid, 30 parts of acrylic acid and a solution of 1.5 parts of azo-bis-isobutyronitrile in 100 parts of ethyl acetate are mixed cold and then heated to reflux temperature in a flask provided with stirrer and reflux condenser on a water bath. This temperature is maintained for 6 hours, during which time the polymer precipitates in finely distributed form. After cooling, it is filtered off, washed with ethyl acetate and dried under reduced pressure.

100 Parts of a colourless and flowable powder having a relative specific viscosity of 0.148 are obtained. The phosphorus content is 22.2%.

(b) 200 parts of ethyl acetate are heated to boiling in a flask provided with a stirrer and reflux condenser. A solution of 100 parts of vinyl-phosphonic acid, 100 parts of acrylic acid, 1 part of azo-bis-isobutyronitrile and 200 parts of ethyl acetate is then added dropwise in the course of 2 hours, and the mixture heated for 4 hours under reflux. The polymer that precipitates is filtered off, washed as described in (a) above and dried. Yield: 190 parts, relative specific viscosity 0.232, phosphorus content 13.6%.

(c) When operating in a manner analogous to that described under (b) but using 3 parts of azo-bis-isobutyronitrile, a polymer is obtained having a relative specific viscosity of 0.170.

(d) When operating in a manner analogous to that described under (b) but using 6 parts of azo-bis-isobutyronitrile, a polymer is obtained having a relative specific viscosity of 0.134.

(e) A solution of 90 parts of vinyl-phosphonic acid, 210 parts of acrylic acid, 4.5 parts of azo-bis-isobutyronitrile and 500 parts of ethyl acetate is added dropwise, in the course of 2 hours, in a manner analogous to that described under [b], to 500 parts of boiling ethyl acetate. After being heated for 4 hours under reflux, the mixture was cooled,

filtered and the precipitate was washed and dried. Yield: 285 parts. Relative specific viscosity: 0.266.

5 A composition according to the invention may additionally comprise other components conventionally used in the manufacture of washing and cleansing compositions, for example, one or more bleaching agents, sulphates, soluble silicates, cellulose derivatives, preferably mixtures of sodium carboxymethyl cellulose, optical brighteners, perfumes or dye-stuffs.

10 As anionic surfactants, of which more than one may be used, there may be mentioned, for example, synthetic sulphates and sulphonates which lower the surface tension. Carriers of the surface tension lowering activity are aliphatic hydrocarbon radicals which may be bonded directly or indirectly to the sulphate or sulphonate group. Alkylbenzene-sulphonates having a straight or branched alkyl chain having from 10 to 20 carbon atoms, alkane-sulphonates having from 10 to 20 carbon atoms and saturated or unsaturated fatty alcohol sulphates having from 10 to 18 carbon atoms, are advantageously used. Fatty acid amides of taurine or of methyl-aurine and the sulphates of fatty alcohol polyglycol ethers which may be prepared by the addition of ethylene or propylene oxide to fatty alcohols may also be used.

15 In addition to anion-active surfactants, there may also be used soaps, i.e. the alkali metal salts of fatty acids having from 10 to 20 carbon atoms.

20 The non-ionic surfactants which may be used are, for example, the products obtained by the addition of from 4 to 25 mols of ethylene oxide to alkylated phenols having a straight or branched alkyl chain having from 6 to 12 carbon atoms, to aliphatic alcohols having from 8 to 18 carbon atoms and to fatty amines having from 8 to 18 carbon atoms. As non-ionic surfactants there may also be used condensation products of ethylene oxide and propylene oxide, which have a foam-reducing action.

25 In the washing and cleansing compositions of the invention, the proportion by weight of polymer salt to surfactant is, in general, in the range of from about 1 : 3 to 10 : 1, preferably from 1 : 2 to 5 : 1.

30 Solutions of washing and cleansing compositions containing builders according to the present invention may be adjusted to pH-values in the range of from about 6 to 12, preferably from 9.5 to 11.5.

35 The polymer compounds used according to the present invention have a good solubility in water and are clearly superior to the condensed phosphates with regard to their stability to decomposition. It is assumed that this stability results from the fact that the polymer compounds unlike condensed phosphate do not

contain a P—O—P bond which is susceptible to hydrolysis.

Also the organic polymer compounds, in comparison with sodium-tri-polyphosphate, either alone or in combination with surfactants, show distinctly better cleansing effects, especially at low concentrations.

Furthermore, the phosphorus content, compared with sodium tri-polyphosphate, is considerably lower, especially in the case of the copolymers of vinyl-phosphonic acid and acrylic acid.

The following Examples illustrate the invention. The polymer compounds according to the invention are used in form of the acids and are converted in the solution into the corresponding salts.

Example 1

An aqueous washing bath was prepared from:

2.00 g/l of polyvinyl-phosphonic acid having a monomer content of 10% by weight, a relative specific viscosity of 0.070 (prepared according to the method described under (a)),
1.50 g/l of potassium hydroxide,
0.50 g/l of sodium dodecyl-benzene-sulphonate (having a straight chain alkyl radical),
0.25 g/l of an addition product of 10 mols of ethylene oxide and 1 mol of nonylphenol,
0.15 g/l of tallow fat soap (sodium salt of a mixture of fatty acids having about 16 to 18 carbon atoms),
0.30 g/l of sodium meta-silicate,
0.15 g/l of magnesium silicate,
0.55 g/l of sodium sulphate,
0.10 g/l of sodium carboxymethyl cellulose.

With this bath, very good cleansing effects are obtained already at a washing temperature of 60°C.

In the above detergent solution, there may be used with practically the same result, instead of the above-mentioned copolymer, a copolymer of 30% by weight of vinyl-phosphonic acid and 70% by weight of acrylic acid (relative specific viscosity 0.266; prepared according to process b) described above) or a copolymer of 50% by weight of vinyl-phosphonic acid and 50% by weight of acrylic acid (relative specific viscosity 0.170; prepared according to the process described under c)).

Example 2

An aqueous all purpose cleansing bath having a good cleansing action contains the following components:

1.00 g/l of copolymer of 30% by weight of vinyl-phosphonic acid and 70% by weight of acrylic acid (relative specific viscosity 0.266; prepared according to method c)),
1.00 g/l of monoethanol-amine,
1.00 g/l of sodium dodecyl-benzene-sulphonate (containing a straight chain alkyl radical),

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0.15 g/l of an addition product of 10 mols of ethylene oxide and 1 mol of nonylphenol, 0.10 g/l of an addition product of 10 mols of ethylene oxide and 1 mol of a $C_{14}-C_{18}$ fatty acid mono-ethanol-amide.

Example 3

A washing bath which is especially suited for the washing of synthetic fabrics has the following composition:

1.00 g/l of a copolymer of 50% by weight of vinylphosphonic acid and 50% by weight of acrylic acid (relative specific viscosity 0.232, prepared according to method b)),

0.70 g/l of sodium hydroxide,

0.35 g/l of an addition product of 8 mols of ethylene oxide and 1 mol of a $C_{14}-C_{18}$ fat alcohol;

0.25 g/l of an addition product of 5 mols of ethylene oxide and 1 mol of iso-tridecyl alcohol;

1.85 g/l of sodium sulphate,

0.80 g/l of sodium carboxy-methyl cellulose,

0.02 g/l of methyl-hydroxyethyl cellulose.

Instead of the mentioned copolymer, there may also be used with good success a copolymer of 80% by weight of vinylphosphonic acid and 20% by weight of acrylic acid (relative specific viscosity 0.124; prepared according to method a) as a component of the washing bath.

Example 4

In washing tests, specimen of an artificially soiled cotton test fabric (WFK-fabric) were washed for 30 minutes at 95°C in a laboratory test apparatus (type Linitest of Messrs. Quarz-lampen GmbH, Hanau) with highly active washing baths.

The washing bath containing builders according to the invention had the following composition:

1.00 g/l of a copolymer of 50% by weight of vinyl-phosphonic acid and 50% by weight of acrylic acid (relative specific viscosity 0.134; prepared according to method d) described above);

0.70 g/l of sodium hydroxide,

0.50 g/l of sodium alkane-sulphonate (straight chain C_{12} to C_{18} alkane sulphonate, main constituent C_{14} to C_{17} alkane sulphonate),

0.25 g/l of an addition product of 11 mols of ethylene oxide and 1 mol of a $C_{14}-C_{18}$ fat alcohol,

0.15 g/l of tallow fat soap (sodium salt of a mixture of fatty acids having about 16 to 18 carbon atoms),

0.20 g/l of sodium meta-silicate,

0.20 g/l of magnesium silicate,

0.20 g/l of sodium carboxy-methyl cellulose,

1.00 g/l of sodium perborate-tetrahydrate.

For comparison, washing baths were tested

which had otherwise the same composition but

a) which contained, instead of the copolymer of vinylphosphonic acid and acrylic acid, 1.00 g/l of a polymaleic acid anhydride having

a relative specific viscosity of 0.080 (measured with free polymaleic acid with a 1% solution in dimethylformamide at 20°C) and 0.80 g of sodium hydroxide,

b) which did not contain builders (blind test).

The degrees of re-emission of the test fabrics were measured photometrically prior to and after the washing operations. The degrees of re-emission are expressed in %, referred to a standard value. The difference between the re-emission degrees measured prior to and those obtained after the washing represents a measure of the cleansing effect produced by the washing operation.

With the washing bath according to the invention, the difference between the re-emission degrees was found to be 34, whereas with the washing bath a), which contained the sodium salt of polymaleic acid, a value of 28 was obtained and in the blind test without builders a value of 14 was determined. The above test values distinctly show the superior builder action of the polymer compounds of the invention over that of the sodium salt of polymaleic acid.

Example 5

The washing effects of the polymer compounds used according to the invention and of sodium tri-polyphosphate were compared. The products were tested I) alone without additives, and II) in combination with a mixture of surfactants.

For this test, specimen of artificially soiled cotton test fabric (WFK fabric) were washed for 30 minutes at 95°C in a laboratory test apparatus (type Linitest of Messrs. Quarz-lampen GmbH, Hanau).

For preparing the washing baths, the polymer compounds in form of their free acids were dissolved in quantities of 0.6, 1.0 and 1.4 g/l of water having a hardness of 15° (German hardness) and combined with the equivalent amount of sodium hydroxide solution. In the test of the builders in combination with surfactants (test series II), the washing baths additionally contained 0.50 g/l of sodium alkane-sulphonate (straight chain $C_{12}-C_{18}$ alkane-sulphonate main constituent $C_{14}-C_{17}$ alkane sulphonate) and 0.25 g/l of an addition product of 11 mols of ethylene oxide and 1 mol of a $C_{14}-C_{18}$ fat alcohol. The pH-value of all baths was adjusted to 10.

The degrees of re-emission of the test fabrics were measured photometrically prior to and after the washing operations. The degrees of re-emission are expressed in %, referred to a standard value. The difference between the re-emission degrees obtained prior to and those obtained after washing which serves as a measure for the cleansing effect produced by the washing, are compiled in the following Tables I and II.

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TABLE I

Builders without surfactant

Builder	Difference between the re-emission degrees measured prior to and those measured after the washing operation, with a builder content of		
	0.6 g/l	1.0 g/l	1.4 g/l
Polyvinyl-phosphonic acid containing 10% of vinyl- phosphonic acid, relative specific viscosity 0.070	6	12	14
Copolymer of 90% by weight of vinyl-phosphonic acid and 10% by weight of acrylic acid, relative specific viscosity 0.090	8	11	12
Copolymer of 70% by weight of vinyl-phosphonic acid and 30% by weight of acrylic acid, relative specific viscosity 0.148	6	10	11
Copolymer of 50% by weight of vinyl-phosphonic acid and 50% by weight of acrylic acid, relative specific viscosity 0.134	15	18	18
Copolymer of 40% by weight of vinyl phosphonic acid and 70% by weight of acrylic acid, relative specific viscosity 0.266	5	11	15
Sodium tri-polyphosphate	4	6	9
Blind test without builder	2		

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TABLE II

Builders with surfactant

Builder	Difference between the re-emission degrees measured prior to and those measured after the washing operation, with a builder content of		
	0.6 g/l	1.0 g/l	1.4 g/l
Polyvinyl-phosphonic acid containing 10% of vinyl-phosphonic acid, relative specific viscosity 0.070	25	29	29
Copolymer of 90% by weight of vinyl-phosphonic acid and 10% by weight of acrylic acid, relative specific viscosity 0.090	24	26	26
Copolymer of 70% by weight of vinyl-phosphonic acid and 30% by weight of acrylic acid, relative specific viscosity 0.148	21	25	25
Copolymer of 50% by weight of vinyl-phosphonic acid and 50% by weight of acrylic acid, relative specific viscosity 0.134	30	31	31
Copolymer of 30% by weight of vinyl-phosphonic acid and 70% by weight of acrylic acid, relative specific viscosity 0.266	26	29	29
Sodium tri-polyphosphate	16	22	24
Blind test without builder	13		

5 The results distinctly show the superiority of the polymer compounds used according to the invention over sodium tri-polyphosphate, especially at low concentrations.

WHAT WE CLAIM IS:—

10 1. A washing or cleansing composition which comprises one or more anionic surfactants and/or one or more non-ionic surfactants and one or more water-soluble neutral or acid salts of an organic homo- or copolymer containing phosphonic acid groups.

15 2. A composition as claimed in claim 1, wherein the homo- or copolymer also contains carboxylic acid groups.

20 3. A composition as claimed in claim 1, wherein the polymer containing phosphonic acid groups comprises a homo-polymer of vinyl-phosphonic acid or a copolymer thereof with a copolymerisable monomer.

4. A composition as claimed in claim 1 or

claim 2, wherein the polymer containing phosphonic acid groups comprises a copolymer of vinylphosphonic acid with acrylic acid and/or crotonic acid and/or acrylamide.

25 5. A composition as claimed in any one of claims 1 to 4, wherein the water-soluble salt is an alkali metal salt, an ammonium salt or a substituted ammonium salt.

30 6. A composition as claimed in claim 5, wherein the alkali metal is sodium or potassium.

35 7. A composition as claimed in any one of claims 1 to 6, wherein the homo- or copolymer the water-soluble salt of which is used, has a relative specific viscosity, measured in a 5% by weight solution in 10% aqueous sodium chloride solution, of at least 0.020.

40 8. A composition as claimed in claim 7, wherein the homo- or copolymer, the water-soluble salt of which is used, has a relative specific viscosity in the range of from 0.060 to 2.0.

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9. A composition as claimed in any one of claims 4 to 8, wherein the copolymer contains at least 2% by weight of units derived from vinyl-phosphonic acid. 25
- 5 10. A composition as claimed in claim 9, wherein the copolymer contains from 5 to 60% by weight of units derived from vinyl-phosphonic acid. 30
- 10 11. A composition as claimed in claim 10, wherein the copolymer contains from 30 to 55% by weight of units derived from vinyl-phosphonic acid. 35
- 15 12. A composition as claimed in any one of claims 1 to 11, having a pH in the range of from 6 to 12. 40
- 20 13. A composition as claimed in claim 12, having a pH in the range of from 9.5 to 11.5.
14. A composition as claimed in claim 1, which comprises a water-soluble neutral or acid salt of a homo- or copolymer which has been prepared by a process substantially as described herein.
15. A composition as claimed in any one of claims 1 to 14, wherein the weight ratio of homo- or copolymer to surfactant is in the range of from 1:3 to 10:1.
16. A composition as claimed in claim 15, wherein the weight ratio of homo- or copolymer to surfactant is in the range of from 1:2 to 5:1.
17. A composition as claimed in any one of claims 1 to 16, which additionally comprises one or more bleaching agents, sulphates, soluble silicates, cellulose derivatives, optical brighteners, perfumes, or dyestuffs.
18. A composition as claimed in claim 1, substantially as described in any one of Examples 1 to 5 herein.
19. A washing or cleansing process, wherein a composition as claimed in any one of claims 1 to 18 is used.

ABEL & IMRAY,
Chartered Patents Agents,
Northumberland House,
303-306 High Holborn, London, W.C.1.

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